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Recovery of tailings from the vanadium extraction process by carbothermic reduction method: Thermodynamic, experimental and hazardous potential assessment

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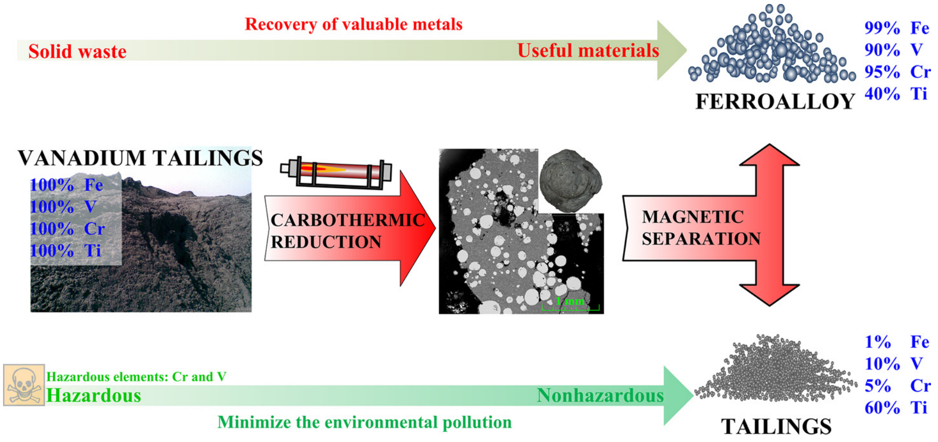
GRAPHICAL ABSTRACT



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ABSTRACT

A cleaner process is tremendously required to deal with the vanadium tailings, which may cause serious environmental problem due to the high content of water soluble hazardous elements such as V and Cr. This problem can be possibly solved by proposed high temperature reduction–magnetic separation process, in which, V, Cr and Fe can be recycled as ferroalloy. The thermodynamic calculation results reveal that a higher temperature (> 1127.8 °C) promotes the reduction of Fe, V and Cr, and improves the recovery rates of V and Cr in liquid iron. The reduction behavior of vanadium tailings was investigated using XRD, TG/DSC, SEM, EDS and ICP-OES techniques. The EDS results show that a small portion of V was remained in the slag phase when roasted at 1300 °C, while nearly all of V and Cr can concentrate in ferroalloy at 1400 °C. Approximatly 90% of V and 95% of Cr recovery in magnetic fraction can be obtained for the magnetic separation step. A small portion of V and Cr is remained in the non-magnetic final tailings, however, the hazardous potential assessments results indicate that such kind of tailings can safely use as secondary materials or stockpiled as an end-waste.

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1. Introduction

Vanadium bearing slag from the LD converter is the main raw materials for the production of vanadium in China. Recent data from the U.S. Geological Survey (2016) indicated that more than half of vanadium in the word is supplied by China (about 42,000 metric tons of vanadium) [1]. Approximately 200 tons of tailings were generated per ton of produced vanadium pentoxide (V_2O_5). More than 1.2 million tons of such tailings ("vanadium tailings" is used hereafter) are annually generated from the vanadium industry in China [2]. The enormous vanadium tailings dumped in landfills or stockpiled year by year, and only a small amount is recycled [3]. The disposal of vanadium tailings does not only occupy large extent of land and waste valuable metal, but also cause ecological problems [3]. Vanadium tailings contain relatively high amounts of chromium (Cr), which is a well-known carcinogenic substance when in oxidation state of +6 [4]. Soluble forms of vanadium in the vanadium tailing also pose a serious environmental problem. A number of oxides of vanadium are regarded as class I-II hazardous agent and have harmful effects on the human organism [5,6].

In the past decades, a considerable number of investigations were focused on recycling of vanadium tailings as summaries in Table 1. Vanadium tailings can be used to produce geopolymers [7,8], V-Ti black ceramic [9,10], far-infrared radiation coatings [11], but only very small part of tailings were used every year. Vanadium tailings also can be utilized to recover residual vanadium by NaOH sub-molten salt leaching [12] or acid leaching process [13] due to its relatively high content of vanadium. However, the extraction of vanadium from secondary slag consumes high energy since it needs multiple roasting and leaching. Furthermore, the leaching residue is still a tough thing for cleaner production.

The most abundant metal in the vanadium tailings is iron, and its recovery was investigated by many researchers. It was reported that vanadium tailings can be recycled in a blast furnace or electric furnace [16,17]. However, the hazardous element Cr can be accumulated in hot metal and converter slag that may cause more serious environmental problem. Furthermore, the reduction of Cr_2O_3 is strongly endothermic process, which requires extra heat consumption and consequently leads to a higher coke rate [18]. High content of alkaline oxides such as Na_2O and K_2O may not only worsen the operation of reduction but also lead to accelerating the erosion of refractory materials. A coal based reduction-magnetic separation process also used to recover iron from vanadium tailings at temperature of 1200 °C. However, the metallic iron particles are too small to achieve a high magnetic separation index without a high intensity grinding. Moreover, instead of recycling, Cr and V were enriched in the non-magnetic part [14].

In our previous study, calcification roasting-acid leaching process was used to deal with the vanadium –bearing converter slag, and the vanadium tailings contains very low content of alkaline oxides but high content of calcium [19]. The present authors also have already verified both iron and the hazardous elements of Cr and V can be recovered as the ferroalloy by high temperature reduction-magnetic separation process. Furthermore, titanium will enrich in the reduction residue which can be used as raw materials for the production of titanium dioxide [15]. However, the mechanism of the reduction process for such kind of vanadium tailings is unknown and less studied. The hazardous potential of such reduction residue stored in the slag dump is also unknown. Hence, the carbothermic reduction behavior of vanadium tailings and the hazardous potential of the solid wastes were investigated in this study.

2. Experimental

2.1. Materials

Vanadium tailings used in this work was obtained in bench scale

Table 1
Summary of previous works on recycling of vanadium tailings.

Origin	Chemical composition (%)	Mineralogy	Methods and Parameters	Products	Ref
Hubei in China	Si 28.9, TFe 2.88, Ti 0.28, V 0.24, Na 1.97	Quartz, Feldspar, Plaster, Hematite	Mixing with metakaolin or fly ash and grinded to fines	Ordinary or fire-resistant geopolymers	[7,8]
NA	TFe 41.45, Ti 4.38, Si 9.0, Mn 4.21, V 0.73, Cr 0.73, Na 2.82	Hematite, V_2O_3, V_2O_5	Mixing-drying-calcination: Mixing (65% Vanadium tailings + 25% Kaolin + 15% Earthenware clay); Grinding (< 125 μm); Drying (100 °C, 2 h); Calcination (1210 °C, ~15 min)	V-Ti Black ceramic	[9,10]
Panzhihua in China	TFe 31.64, Ti 6.6, Si 6.72, Mn 5.58, V 1.4, Cr 1.3, Na 4.01	NA	Calcination-grinding-mixing: Calcination (1200 °C, 3 h), grinding (< 50 μm), mixing (vanadium tailings + dispersant + agglutinant + hardener + defoamer)	Far-infrared radiation coatings (Normal total emissivity 0.84)	[11]
Chengde in China	TFe 33.0, Ti 7.17, Si 8.59, Mn 3.77, V 0.98, Cr 2.96, Na 5.1	Hematite, psudobrookite, acmite	NaOH sub-molten salt leaching: 170 °C, 3 h, NaOH/Vanadium tailings mass ratio 4:1, < 74μm	Vanadium leaching ratio 93%,	[12]
Panzhihua in China	TFe 31.33, Ti 7.55, Si 6.82, Mn 6.03, V 0.99, Cr 1.47, Na 3.78	NA	Acid leaching: H_2SO_4 150 g/L, HF 30 g/L, L:S = 5:1, $KMnO_4$ 3.33%, 85 °C, 4h	Vanadium leaching ratio 82.86%	[13]
NA	TFe 36.54%, Ti 5.57, Si 6.37, V 0.54, Cr 1.23, Mn 3.52, Na 2.6	Hematite, psudobrookite, acmite	Reduction–magnetic separation: Mixed with 30% lignite and 10% CaO, 1200 °C, 60 min, reduction products < 30 μm.	Magnetic concentrate (TFe 90.31%, recovery rate TFe 83.88%)	[14]
Panzhihua in China	TFe 31.85%, Ti 8.94, Si 9.2, V 0.48, Cr 1.05, Mn 3.76, Ca 4.8	Hematite, psudobrookite,	Reduction-magnetic separation: carbon addition ~12%, 1300 °C, 60 min.	High Cr-V-Fe (recovery rate TFe 96.34%, V 79.26%, Cr 82.81%), Ti-bearing slag (recovery rate Ti 93.51%)	[15]